SYNTHESIS AND CHARACTERIZATION OF PLATINUM DOPED TITANIA AND SILVER DOPED TITANIA FOR PHOTO-CATALYTIC DEGRADATION OF PRE-TREATED PALM OIL MILL EFFLUENT

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ABSTRACT

In this study, the potential of application of photo-catalytic degradation of palm oil mill effluent (POME) using metal-doped TiO_2 was explored. The study comprised of synthesis and characterization of TiO_2 based photo-catalysts doped with platinum (Pt) and silver (Ag) to widen the light absorption spectrum. The aim was to study the effect of photo-catalytic degradation of the pre-treated POME. The experiment was carried out under the UV and visible light and monitoring the COD degradation of pre-treated POME. Various factors affecting the photo-catalytic performance such as metal loadings and photo-catalyst loading were investigated to determine the best operating conditions for POME treatment. Physicochemical characterization studies showed that both Pt/TiO_2 and Ag/TiO_2 have mesopores structure with BJH pore diameter ranged from 11.0 to 20.0 nm. Moreover, the catalysts possessed low BET specific surface area (7.0 to 12.0 m^2/g) with the surface morphology also captured by the FESEM images. XRD diffractogram proved that the high temperature did not alter the crystalline structure of catalysts as well as the phase which was retained in anatase phase. The absorption of spectrum in visible range by Ag/TiO_2 was confirmed by UV-vis DRS. Results have shown that, for metal loading effects employing a minimum 0.2 g/L of photocatalyst, it can be concluded that the 0.50 wt% Pt and 0.50 wt% Ag loadings yielded the best performance with the highest apparent specific reaction rate, k_{app}, obtained from the first-order Power law modelling under the irradiation of UV and visible light, respectively. In addition, the studies pertaining to the effects of photocatalyst loadings over the 0.50 wt% Pt/TiO_2 and 0.50 wt% Ag/TiO_2 photocatalysts showed that 1.0 g/L of Pt/TiO_2 was the optimum loading whilst for the Ag/TiO_2, optimum loading was at 1.5 g/L. The photo-catalytic degradation process using both platinum doped titania and silver doped titania is the ideal solution for pome treatment. This finding should be useful in design, operation, optimization and control of photo-catalytic degradation process. For future works, other types of visible-light responsive catalysts can be employed with some in-situ activity characterizations using sophisticated equipment with various process temperatures.

ABSTRAK

Dalam kajian ini, potensi penggunaan foto-pemangkin menggunakan logam didopkan dengan titania (TiO_2) untuk proses degradasi sampel sisa buangan/ atau enap cemar kilang kelapa sawit (POME). Kajian ini merangkumi sintesis dan pencirian TiO_2 berdasarkan foto-pemangkin yang didopkan dengan logam platinum (Pt) dan perak (Ag) untuk meluaskan penyerapan spektrum cahaya oleh foto-pemangkin. Tujuannya adalah untuk mengkaji keberkesanan foto-pemangkin terhadap proses degradasi sampel POME yang telah melalui proses pra-rawat. Eksperimen telah dijalankan di bawah sinar ungu (UV) dan cahaya yang boleh dilihat menggunakan foto-pemangkin yang telah didopkan dengan Pt dan Ag dengan memantau proses perubahan bacaan nilai permintaan oxygen kimia (COD) sampel POME yang telah melalui prosess pra-rawat. Pelbagai faktor yang mempengaruhi prestasi foto-pemangkin seperti peratusan berat logam yang didopkan dalam TiO_2 dan jumlah foto-pemangkin yang digunakan telah disiasat untuk menentukan keadaan operasi yang terbaik untuk rawatan sampel POME. Kajian pencirian fizikokimia menunjukkan kedua-dua Pt/TiO_2 dan Ag/TiO_2 mempunyai struktur berliang pertengahan dengan diameter BJH daripada 11.0 hingga 20.0 nm. Selain tu, kesemua katalis mempunyai keluasan permukan khusus BET yang rendah dari 7.0 hingga 12.0 m^2/g yang juga ditunjukkan oleh gambar FESEM. Belauan XRD membuktikan bahawa suhu yang tinggi tidak mengubah struktur dan juga fasa anatase (bentuk kristal) foto-pemangkin. Penyerapan foto-pemangkin terhadap spektrum dalam julat cahaya yang boleh dilihat oleh Ag/TiO_2 disahkan oleh keputusan analysis dari UV-vis DRS. Keputusan analisis telah menunjukkan bahawa, untuk kesan beban logam yang menggunakan beban minimum 0.2 g/L foto-pemangkin, 0.50% berat Pt dan 0.50% berat Ag beban memberikan prestasi yang terbaik di bawah sinar UV dan sinar cahaya yang boleh dilihat, dengan kadar reaksi tertentu tertinggi, k_{app}, yang diperolehi dari model reaksi pertama iaitu Power Law. Disamping itu, kajian mengenai kesan kepekatan foto-pemangkin ke atas 0.50% berat Pt/TiO_2 dan 0.50% berat Ag/TiO_2 menunjukkan bahawa 1.0 g/L Pt/TiO_2 adalah kepekatan yang optimum manakala bagi Ag/TiO_2, kepekatan yang optimum adalah pada 1.5 g/L. Proses degradasi foto-pemangkin menggunakan kedua-dua Pt/TiO_2 dan Ag/TiO_2 adalah penyelesaian yang ideal untuk proses rawatan POME. Penemuan ini adalah sangat berguna dalam reka bentuk, operasi, pengoptimuman dan kawalan proses degradasi foto-pemangkin. Untuk

kajian dimasa hadapan, pelbagai jenis pemangkin cahaya boleh digunakan dengan beberapa pencirian secara in-situ menggunakan peralatan canggih dalam pelbagai julat suhu.

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LIST OF NOMECLATURES

Ag	Silver Metal
Ag/TiO_2	Silver doped Titanium Dioxide
$AgNO_3$	Silver Nitrate
CO_2	Carbon Dioxide
Degussa P25	Commercial Titanium Dioxide, Brands Degussa
H_2	Hydrogen
H_2O	Water
H_2PtCl_6	Chloroplatinic Acid
eV	Binding Energy
m^2/g	Meter Square per Gram
m^3	Volume in Meter Cubic
mg/L	Density in Milligram per Liter
N_2	Nitrogen
O_2	Oxygen
K	Temperature Unit in Kelvin
ppm	Concentration Unit in Part Per Million
Pt	Platinum Metal
Pt/TiO_2	Platinum Doped Titanium Dioxide
Ti	Titanium
TiO_2	Titanium Dioxide
wt%	Weight Percent
^oC	Degree Celsius
%	Percent
λ	Wavelength (nm)
θ	Theta Degree

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett- Teller
BJH	Barrett, Joyner and Halenda
BOD	Biological Oxygen Demand
CB	Conduction Band
COD	Chemical Oxygen Demand
EHPs	Electron-Hole Pairs
EQA	Environmental Quality Act
FESEM	Field Electron Scanning Electron Microscopy
HRT	Hydraulic Retention Time
MB	Methylene Blue
MPOB	Malaysian Palm Oil Board
MT	Metric Tonne
NIR	Near Infra-red
NUV	Near Ultra-violet
POME	Palm Oil Mill Effluent
UV	Ultra Violet
UV-vis	Ultra Violet -Visible Spectrometer
VB	Valence Band
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

As society becomes more affluent, environmental issues associated with the treatment of pollutants in air and water has increasingly thrown into the limelight. Consequently, the regulations concerning the industrial effluent in particular, have been tightened and loopholes fixed to mitigate the ill-effects towards the environment for the sake of conservation of the Mother Nature for future generations.

Significantly, one of the largest water polluters in Malaysia originates from oil palm plantation sector. Not only that Malaysia is home to the one of the largest oil palm plantation in the world, it is also the second largest producer of palm oil globally, behind only to the Indonesia with annual production of 17 million tons of palm oil from 4.9 million hectares of planted area with reported export earnings of RM62 billion (Government Transformation Program, 2011). Currently, there are circa 425 active palm oil mills in Malaysia that collectively produce palm oil mill effluent, also known as POME (a thick brownish wastewater rich in organic pollutants) (Official Portal Of Malaysia Palm Oil Board. 2012). It is further estimated that 1.5 m^3 of water are required to process a ton of fresh fruit bunch whereby half of the amount becomes POME (Kongnoo et al., 2012).

To alleviate disastrously irreversible damage to the aquatic ecology, the regulation requires that the POME to be treated before being discharged to the watercourse. Specifically, the regulatory control over discharges from palm oil mills is in-scripted in the Environmental Quality (Prescribed Premises) (Crude Palm Oil)

Regulations, 1977 promulgated under the Environmental Quality Act, 1974 and fallen under the jurisdiction of the Department of Environmental (DOE). It is a well-known fact that the fresh POME is acidic with pH ranged from 4 to 5, chemical oxygen demand (COD) of 40,000 to 100,000 mg/L and biological oxygen demand (BOD) of 25,000 to 65,000 mg/L (Official Portal Of Malaysia Palm Oil Board. 2012; Zinatizadeh et al., 2006; Wu et al., 2007, Choorit and Wisarnwan, 2007). The most common practice uses aerobic ponding system due to its low capital and operating costs. Unfortunately, this method is land-intensive and requires long hydraulic retention time (HRT), typically about 1 to 2 months (Ma et al., 1993).

Recent advances in the area of light-activated catalysts suggest that one of the promising technologies for the destruction of organic pollutants is the application of semiconductor photo-catalysts. In particular, two types of light spectrum have been explored *viz*. UV spectrum (200 to 400 nm) and visible light spectrum (400 to 700 nm) as the activators. Due to the different wavelength, material selection is critical in ensuring light energy can be absorbed by the photo-catalyst. Significantly, the TiO_2 photo-catalyst has been widely employed to degrade organic solution, referenced herein (Patsoura et al., 2007; Jauregui et al., 1998; Mills and Le Hunte, 1997). Nevertheless, due to wide band gap (~3.3 eV), TiO_2 can only absorb UV light, which only represents about 5% of our solar spectrum. In contrast, the visible light spectrum accounts for circa 46%.

A flurry of research activities have been undertaken to address this issue via two different strategies; either researching new materials to substitute the TiO_2 or to incorporate dopants into the TiO_2 matrix to widen the light spectrum in order to cover the visible light. Specifically, this work focuses on doping of TiO_2 with the platinum (Pt) and also silver (Ag) for photo-degradation of POME. The characterization of Pt/TiO_2 and Ag/TiO_2 photo-catalysts were also carried out to determine the physicochemical properties and the relationship with the photo-catalytic performance.

1.2 PROBLEM STATEMENT

POME is a highly polluting wastewater that originates from palm oil mills. Most of the mills have employed open ponding system to treat the POME. However, this conventional treatment requires long hydraulic retention time (HRT). Moreover, it requires vast land which otherwise can be earmarked for better utilization.

The degradation of organic pollutants over light-activated photo-catalysts has been increasingly acknowledged as one the most interesting areas. The titanium dioxide (TiO_2) photo-catalyst has been recognized as effective material for degrading organic matter under the UV-light. Nonetheless, it is ineffective under visible-light; hence necessitates the incorporation of dopant to increase its light spectrum to function under the visible light for degrading organic pollutant, in this work, POME.

1.3 OBJECTIVES OF RESEARCH

The objectives of this research work are:

(i) To synthesis and characterize platinum doped titania (Pt/TiO_2) and silver doped titania (Ag/TiO_2) photo-catalysts to widen light absorption spectrum.

(ii) To study the photo-catalytic degradation of the pre-treated palm oil mill effluent (POME).

1.4 SCOPES OF RESEARCH

To achieve the outlined objectives, the following scopes were investigated:

- The Pt/TiO_2 and Ag/TiO_2 photo-catalysts were synthesized via alcohol reduction technique from chloroplatinic acid (H_2PtCl_6) and Silver Nirate ($AgNO_3$) as salt-precursors, respectively.

- The physicochemical properties of the synthesized catalysts were characterized using methods such as XRD, N_2 physisorption, FESEM imaging, UV-Vis diffuse reflectance and XPS.

- The photo-activity of the synthesized photo-catalysts was investigated via photoreaction of Methylene Blue, a commonly employed organic dye.

- As the degradation of POME involved chemical pathway, therefore the efficiency of photo-degradation was measured in terms of COD values:

  (i) Photo-catalytic activity under the UV and also visible light irradiation for dopants comprised of Pt and Ag.

  (ii) Various metal loadings (0, 0.25, 0.5 and 1.0 wt% of Pt and Ag doped on TiO_2).

  (iii) Various photo-catalyst loadings to the reaction medium (blank, 0.2, 0.5, 1.0, 1.5 and 2.0 g/L of photo-catalysts).

1.5 SIGNIFICANCE OF STUDY

An application of photo-catalysis for the degradation of organic compound could be a successor to the conventional treatment of POME. Fast growth in oil palm plantation especially in Malaysia generates vast amount of POME every day that requires treatment. Significantly, the average of 12 hours sunlight harnessed per day provides an ideal energy source for the application of photo-catalytic process. Clearly, this work serves as a “baseline” investigation to determine the photo-catalytic degradation of POME under a controlled light-simulated environment. Therefore, the novelty of the current study lies in the finding of an ideal photo-catalyst which is applicable for degradation of POME under both the visible and/or near UV light energy.

1.6 ORGANIZATION OF THESIS

This thesis is structured as follows:

- Chapter 2 summarizes the literature review on POME production from palm oil mills. A review about photocatalysts and also existing works on organic pollutant phototreatments are also included.

- Chapter 3 presents the materials and methods employed in this work including the source of raw materials and chemicals. Type of equipment, experimental methods and analysis procedures are also presented in details.

- Chapter 4 discusses the results from the current work, which includes three main sections namely photocatalyst characterization, methylene blue activity testings as well as pre-treated POME photo-degradation studies.

- Chapter 5 provides the concluding remark and directions for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 OVERVIEW OF CHAPTER

In this chapter, a comprehensive review of literature will be presented. The first part discusses the growth of palm oil industry in Malaysia, the effect of POME to environment and humans, and the latest technology for POME treatment. Besides, this part also describes the possibility of photo-catalysis process to degrade the waste. The second section elaborates the advantages of TiO_2 as photo-catalyst. Finally, the third part presents the working principles of photo-catalysis, different types of photo-catalysts, structural properties of photo-catalysts and photo-catalytic performance comparison between commercial Degussa P25 TiO_2, and TiO_2-based photo-catalysts doped with platinum (Pt) and silver (Ag), synthesis methods of both metal dopants and discussion of main parameters that normally affect the photo efficiency.

2.2 PALM OIL MILL EFFLUENT IN MALAYSIA

Palm oil is one of the most rapidly-grown equatorial crops and occupies the largest plantation area in Malaysia. Approximately 17.0 MT of annual crude palm oil was produced in 2010, worth some RM60 billions with an average market price of RM3000 per tonne (Official Portal Of Malaysian Palm Oil Board, 2014). Unfortunately, masked behind the success stories is the burgeoning generation of organic waste.

To put it into context, for every ton of crude palm oil extracted, around 2.4 cubic meter of POME is produced (Subramiam, 2011). Moreover, the waste is normally at temperatures of 353 to 363 K when discharged into the ponds (Rupani et al., 2010).

Table 2.1 shows the characteristic of POME discharge (Ma, 2000). As can be seen, POME is characterized by high COD and BOD values (50000 and 25000 g/L, respectively).

Table 2.1: The characteristic of POME

CHARACTERISTICS OF POME		
Parameter*	**Mean**	**Range**
pH	4.2	3.4 - 5.2
Biological Oxygen Demand	25000	10250 – 43750
Chemical Oxygen Demand	51000	15000 – 100000
Total Solids	40000	11500 – 79000
Suspended Solids	18000	5000 – 54000
Volatile Solids	34000	9000 – 72000
Oil and Grease	6000	130 – 18000
Ammoniac Nitrogen	35	4 – 80
Total Nitrogen	750	180 – 1400

*Units in mg/L except pH

Source: Ma (2000)

The capacity of POME discharged from the mills depends on the operating capacity of the palm oil mill. The estimated amount of POME discharged by the mills with operating time of 22 h per day is summarized in Table 2.2.

Table 2.2: Mill capacity and amount of POME produced.

Capacity (MT / hour)	Volume (m^3 / hour)	Volume (m^3 / day)
20	16	352
30	24	328
45	36	792
60	48	1056
90	72	1584
120	96	2112

Source: Subramaniam (2011)

Several POME treatment pathways have been tested with the details given in Section 2.2.1. However, most of the methods are costly and require long processing period (high hydraulic retention time (HRT)) and focusing more on minimizing the COD and BOD values.

Malaysia is listed as the country that creates the largest pollution load in the river (Vairappan and Yen, 2008). Due to this fact, the palm oil industry faces the challenge of balancing the environmental protection, its economic viability and sustainable development. A huge amount of palm oil mill waste throughout the country needs an efficient treatment and effective disposal technique. Hence, there is an urgent need to continuously search for better ways to preserve the environment while keeping the economy growing.

POME is produced primarily from oil extraction, washing and cleaning process in the mill. The fresh POME is hot (temperature about 353 to 363 K), acidic, thick brownish liquid that contains high concentration of organic matters, high amount of total solids, oil and grease, COD and BOD values. It is considered the most hazardous waste if discharged untreated. Most of the existing palm oil mills conveniently discharge the POME into the man-made ponds (as can be seen in Figure 2.1) for natural degradation of organic pollutant contained inside the POME as the most preferred method of waste water treatment (Rupani, et al., 2010).

(a) (b)

Figure 2.1: (a) Lagoon system for waste water treatment of POME (b) Palm Oil Mill Effluent

Source: Eco-ideal (2012)

The Environmental Quality (prescribed Premises) (Crude Palm Oil) Regulation 1977, promulgated under the enabling powers of Section 51 of the EQA, the governing regulations and regulations and contain the effluent discharge standards. The other regulatory requirements are to be imposed on individual palm oil mills through condition license according to the Environmental Act 1974 (Pierzynski et al., 2005). The effluent discharge standards applicable to crude palm oil mills are presented in Table 2.3.

Table 2.3: The standard discharge of POME

PALM OIL MILL EFFLUENT DISCHARGE STANDARDS						
Parameter*	**Std A 1/7/1978 to 30/6/1979**	**Std B 1/7/1979 to 30/6/1980**	**Std C 1/7/1980 to 30/6/1981**	**Std D 1/7/1981 to 30/6/1982**	**Std E 1/7/1982 to 31/12/1983**	**Std F 1/1/1984 and thereafter**
Ph	5 to 9	5 to 9	5 to 9	5 to 9	5 to 9	5 to 9
Biological Oxygen Demand	5000	2000	1000	500	250	100
Chemical Oxygen Demand	10000	4000	2000	1000	-	-
Total Solids	4000	2500	2000	1500	-	-
Suspended Solids	1200	800	600	400	400	400
Oil and Grease	150	100	75	50	50	50
Ammoniacal Nitrogen	25	15	15	10	150	100
Total Nitrogen	200	100	75	50	-	-
Temperature (°C)	45	45	45	45	45	45

*Units in mg/l except pH and temperature

Source: Official Portal Of Malaysian Palm Oil Board (2014)

2.2.1 POME Treatments

At the initial stage of the oil palm industry, one of the proposed ways for POME disposal is via land application. The disposal of POME on the land results in clogging and water logging of soil. This affects the vegetation on contact. Wood et al. (1979) reported that these problems could be solved by releasing small quantity of POME into the river, since POME is a non-toxic oily waste. Nonetheless, the discharge time is kept short. This is because direct discharge into rivers can cause water pollution (Hwang et al., 1978). Thus, it is necessary to study other treatments which are environmental friendly, lower in cost of operation and has higher efficiency. Several researchers have studied the various aspects of palm oil mill effluent treatment (Ahmad et al., 2000; Azmi and Yonus, 2014; Setiadi et al., 1996; Hameed et al., 2012; Hojjat and Salleh, 2009; Hoon et al., 2001; Fakhru'l-razi and Noor, 1999; Ugoji, 1997).

In a biological treatment, POME is treated physically through several stages such as screening, sedimentation and oil remover prior to the secondary treatment. Hojjat and Salleh (2009) suggested a combined process of acidification pond and flocculation. Both centrifugation and coagulation offer different pretreatment qualities and proven to be better than pretreatment by filtration method. Interestingly, chitosan as a flocculation agent has been effectively employed to remove most of the colloidal and suspended solid in POME, but less efficient in removing dissolved organic matter (Othman et al., 2008). Hameed et al. (2012) reported that the solvent extraction method can be used for the removal of residual oil from POME as pretreatment process. They found that the percentage of extraction of oil from POME increased with increasing mixing time, solvent/feed ratio and mixing rate.

Ponding system is the most conventional method for treating POME. Currently, more than 85 percent of the existing mills employ anaerobic process for POME treatment due to the low cost and easy operating system. Perez et al. (2001) mentioned that ponding system is the most suitable treatment method due to the organic characteristic of POME. Unfortunately, the drawbacks are the requirement of vast land area, relatively long hydraulic retention time (HTR) of 45 to 60 days for the highest effective performance, very bad odor and difficulty in sustaining the liquor distribution

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CHAPTER 3

MATERIALS AND METHODS

3.1 OVERVIEW OF CHAPTER

In this chapter, details of the Pt/TiO_2 and Ag/TiO_2 photo-catalysts preparation are presented followed by the characterization of the photo-catalysts. The characterization techniques include X-ray photoelectron spectroscopy (XPS) for elemental studies, nitrogen physisorption for BET specific surface area and pore size distribution measurements, UV-Vis instrument for band gap energy characterization, field emission scanning electron microscopy (FESEM) for surface morphology capturing and X-ray diffraction (XRD) for crystalline structure scanning. Moreover, the theoretical fundamentals and operational procedures of the catalyst characterization instruments are also presented in this chapter. The last part in this chapter will elaborate the experimental procedures for photo-catalytic degradation studies of methylene blue (MB) dye as and POME. The MB was used in preliminary study to determine the performance of the fabricated photo-catalysts.

3.2 MATERIALS

The chemicals needed in this study are listed in the Table 3.1. All the chemicals listed in Table 3.1 were procured from Sigma-Aldrich. The distilled water was available from the water purification system (brand: Millipore) available in the FKKSA laboratory of Universiti Malaysia Pahang (UMP).

Table 3.1: List of chemicals

Chemical	Purity	Application
Degussa P25 TiO_2	99.5%	Catalyst preparation
Silver nitrate ($AgNO_3$)	99.5%	Catalyst preparation
Chloroplatanic acid (H_2PtCl_6)	40% Pt	Catalyst preparation
Sodium citrate	99.9%	Catalyst preparation
Methanol	40%	Catalyst preparation
Methylene blue	≥ 96%	Photoactivity study
POME	1st pond	Sample study

3.3 SYNTHESIS OF PHOTOCATALYST

Comercial Degussa P25 TiO_2 was altered by metal dopant to extend its photocatalytic ability in visible range. Through this study, platinum (Pt) and silver (Ag) were selected as metal dopants and their performance in photo-catalytic degradation of POME were compared in both UV and visible ranges, respectively. Both H_2PtCl_6 and $AgNO_3$ were used as dopant precursors in preparation of Pt/TiO_2 and Ag/TiO_2 respectively (see Table 3.1).

3.3.1 Preparation of Pt-TiO_2 and Ag-TiO_2 Photocatalysts

All the catalyst preparation procedures in the current work were adapted from the works published by Lin et al. (2006) for the preparation of nano Pt particles from the H_2PtCl_6. The nanoparticles synthesis was conducted in a tri-neck rounded bottom flask with magnetic stirrer and a reflux condenser. The process temperature was controlled using a water bath and thermometer (cf. Figure 3.1). Pt sols were prepared through the reduction of chloroplatinic acid, H_2PtCl_6 by methanol. The separate solutions containing 0.1 M H_2PtCl_6 (aqueous solution) and 0.1 M sodium citrate (J.T. Baker, 99.9 %), respectively, were added to the methanol solution under reflux and stirring at 333 K. The stirring and heating were carried out for 25 min. The reaction was stopped right after the solution turned black. The Pt sols was then added with TiO_2 powder of different weight percentage, wt% (0.25, 0.5 and 1.0 wt% of Pt/TiO_2) in a 500 ml beaker. The mixture was then stirred using an ultrasonic water bath for 8 h at 328 K.

Subsequently, it was dried in an oven at 378 K for 8 h. The resulting white powder was milled and repeatedly washed by distilled water to remove the impurities. The powder was re-dried for 8 h before re-milled. It was finally calcined at 723 K for catalyst characterization and photo-catalytic reaction studies. For the consistency of catalyst synthe sis method for the preparation of Ag nanoparticles (0.25, 0.5 and 1.0 wt% of Ag/TiO_2), the similar procedures as aforementioned were also adopted with the reduction of silver nitrate, $AgNO_3$ by the alcohol.

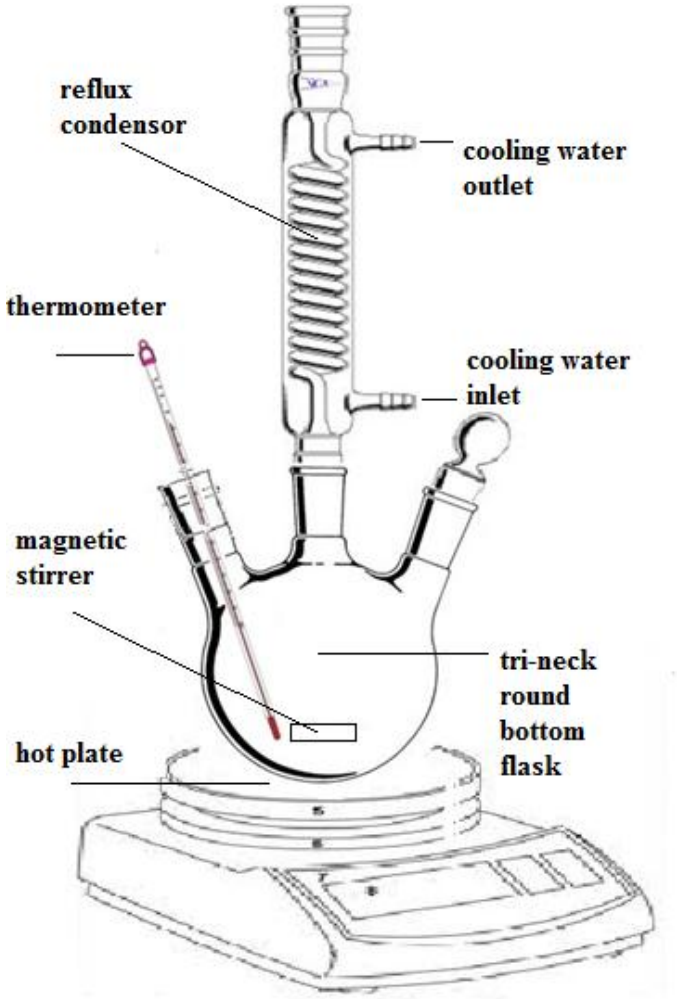

Figure 3.1: Schematic diagram of set up for the preparation of Pt and Ag nanoparticles.